

Artificial photosynthesis: semiconductor photocatalytic fixation of CO₂ to afford higher organic compoundsMichael R. Hoffmann,^a John A. Moss^b and Marc M. Baum^{*b}

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Carbon dioxide is an appealing renewable feedstock for industrial chemical processes. This does not mean, however, that all chemical processes using CO₂ are environmentally-friendly. Perspectives on the sustainability of CO₂ utilization and artificial photosynthesis are provided. The discussions focus on the photocatalytic production of C_x ($x \geq 2$) compounds, where all the carbon in the products is derived from CO₂. This area of research, while promising, has received far less attention than analogous systems leading to C₁ products.

Introduction

Carbon dioxide (CO₂) is an inexpensive, abundant, nontoxic, and renewable resource and therefore constitutes an appealing feedstock for industrial chemical processes. Progress, however, has been hampered by the thermodynamic stability and kinetic

inertness of CO₂, a highly oxidized form of carbon, C(+IV). The environmental importance of this problematic greenhouse gas has fueled a new wave of research on CO₂ activation and chemical fixation over the past decade. Highlights of this progress have been documented in several broad reviews.^{1–3} More specific aspects of CO₂ utilization in synthetic chemistry also have been reviewed and include the carboxylation of organometallic complexes.^{4–6} While these areas of research are of considerable academic interest, they are mostly in their infancy and represent niche opportunities for CO₂ usage.

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for his research and teaching in environmental chemistry and an award for "Creative Advances in Environmental Science and Technology" from the ACS in 2001. He recently served as a Distinguished Visiting Professor at the National Taiwan University and at Tsinghua University in Beijing. Prof. Hoffmann is the organizer of the 19th International Conference on Photochemical Conversion and Storage of Solar Energy, which will take place from 29 July to 3 August 2012 on the Caltech Campus in Pasadena.

Michael R. Hoffmann received a BA in chemistry from Northwestern and a PhD degree in chemistry from Brown University. He was appointed as a professor at Caltech in 1980. Dr Hoffmann has published more than 300 research papers and is the holder of 7 patents leading to recognition from the 'Web of Science' as one of the most highly cited researchers in environmental chemistry. In 1991, he received an Alexander von Humboldt Prize



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where he currently serves as senior faculty. His research interests include semiconductor photocatalysis, photoelectrochemical energy conversion, and spectroscopic methods for investigation of reactions at semiconductor surfaces. His current work in this area is focused on semiconductor-based photocatalytic CO₂ reduction and investigation of naturally-occurring chromophoric compounds with applications in photochemical energy conversion.

John Moss received his B.S. in Chemistry from Davidson College (NC, USA) and his Ph.D. in Inorganic Chemistry from the University of North Carolina at Chapel Hill. Following post-doctoral work with Prof. Michael Hoffmann at Caltech where he investigated surface structure and photocatalytic oxidation mechanisms of TiO₂ semiconductors, he joined the Oak Crest Institute of Science in Pasadena, CA (www.oak-crest.org) in 2001

The potential for large scale CO₂ conversion into value-added materials has been discussed in several review articles. Enthaler *et al.* described the reversible conversion of CO₂ to formic acid by homogeneous, heterogeneous, and biological catalysts with the objective of developing environmentally-friendly hydrogen storage systems.⁷ Dörner *et al.* explored how doped iron catalysts can be used in Fischer–Tropsch chemistry to convert CO₂/H₂ mixtures to energy-rich molecules, notably C₁–C₅₊ hydrocarbons (HCs), in conversion levels as high as 68% at 300 °C.⁸ The authors propose that CO₂ could be converted into CO₂-neutral fuels in a two stage process if a renewable energy source is employed to obtain and convert the reactants. Roy *et al.* surveyed the status of photochemical processes for CO₂/water vapor conversion into HC fuels.⁹ In these solar fuel cells, CO₂ is reduced to a variety of products ranging from alcohols (methanol and ethanol) to HCs (methane, ethane, and ethylene) that hold potential as fuels. Semiconductor photoelectrochemical and photochemical processes are discussed with an emphasis on doped titanium dioxide nanotube arrays.

The above reviews provide an excellent, current survey of the chemistry of CO₂ in a wide range of applications. The present account focuses on semiconductor-catalyzed photolytic processes that afford C_x (x ≥ 2) compounds from CO₂ under mild conditions in an artificial parallel to biological photosynthesis.

Sustainable uses of CO₂

The literature is replete with reports that claim to have developed sustainable, environmentally-friendly, or “green” chemical processes utilizing CO₂ as a key reagent. These claims often are not supported with a discussion of how the new reactions fit into a framework for sustainable usage of the greenhouse gas. Three interrelated aspects of sustainable CO₂ chemistry are presented here – (1) resource usage; (2) potential for net CO₂ fixation; and

(3) potential for CO₂ sequestration- and are discussed in terms of polyurethane production.

The first criterion determining the sustainability of chemical reactions using CO₂ involves *resource utilization* and the value of the product. Important considerations include:

- **Solvent:** Water is preferable over organic solvents, and chlorinated solvents are undesirable due to their toxicity. Supercritical CO₂ is an attractive alternative to water because it can easily be separated from the reaction products and recycled.¹⁰ The omission of a solvent is ideal, although rarely practical,
- **Reagents:** Reactant(s) should be non-toxic, readily-available, renewable, and incorporated into the reaction product,
- **Catalysts:** Toxicity (*e.g.*, Ni, Cd) and scarcity (*e.g.*, Pt, Pd) of catalysts presents a particular challenge in CO₂ activation chemistry,
- **Purification of reaction product(s):** Separation agents should be minimized and chosen based on similar criteria to those described above,
- **Financial and societal value of the product:** Plastics and pharmaceutical building blocks are, for example, more desirable than carbon monoxide (CO).

Most reports on the chemical fixation of CO₂ fall short of meeting these basic principles of green chemistry.¹¹

The potential for net CO₂ fixation is determined by considering the energy inputs and sources in a life cycle analysis (LCA) of the material being produced. Life cycle analysis is a quantitative tool used to evaluate the complete environmental impact of a process or product. The systematic cradle-to-grave approach avoids potential bias resulting from a narrower assessment scope and allows technologies to be compared directly. Recent LCA studies have examined a range of technologies relevant to sustainable energy production including hybrid solar cells,¹² biofuels,¹³ and wind turbines.¹⁴ Biological sinks that fix CO₂ into biomass such as plants and algae are described as carbon neutral. For a commodity to be considered carbon neutral, the CO₂ emissions associated with its production, usage, and disposal must be balanced with either equal carbon fixation in the product, or with CO₂ emission avoidance during the life cycle. Carbon negative processes fix more CO₂ than they emit over their life cycle. Ideally, the entire process is either CO₂ neutral or negative when compared to the Best Available Techniques (BAT). For example, in the heterogeneous catalytic thermochemical conversion of CO₂ to HCs in a FT-like process,⁸ the energy intensity and sources used in the production of the synthesis gas (CO₂/H₂), in the FT process at 300 °C, and in the catalytic conversion of the HC mixture into fuels needs to be evaluated when estimating the potential for net CO₂ fixation.

When touting a new technology for the chemical conversion of CO₂ in the context of rising global atmospheric CO₂ levels it is important to justify the potential impact on CO₂ sequestration or net removal and storage of CO₂ from the atmosphere. Such an analysis needs to take into account the amount of CO₂ captured in the reaction product(s), as well as the timescale over which the carbon is stored before being re-emitted to the atmosphere as CO₂. For example, a solar fuel cell that converts CO₂ to hydrocarbons that, in turn, are used in a combustion process to regenerate CO₂ has the potential of capturing significant amounts of CO₂, but only of storing the carbon for a short period of time. The carbon sequestration value of this technology would be in its CO₂ emission



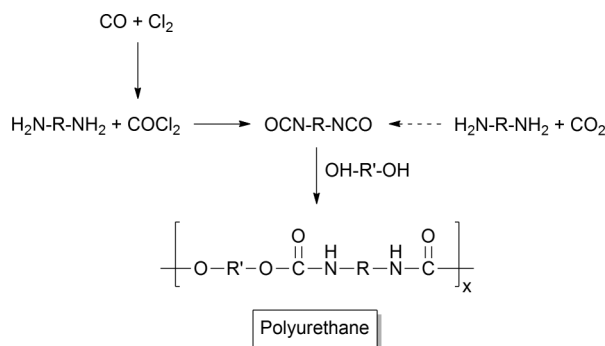
Marc Baum

value materials (*i.e.*, polymers and pharmaceuticals) using homogeneous and heterogeneous catalysis. Within this context, his group currently is working on: the development of catalytic cycles based on low-valent transition metal complexes, CO₂, and unsaturated compounds to afford highly functionalized heterocycles; the investigation of photocatalytic systems in organic synthesis using semiconductors, CO₂, and organic radical traps.

Marc Baum received his doctoral degree in Organic Chemistry from Imperial College of Science, Technology, and Medicine (London, UK). In 1998, he founded the Oak Crest Institute of Science (CA, USA, www.oak-crest.org), a Pasadena-based nonprofit science research organization where he serves as president and senior faculty. He has been a visiting scientist at Caltech since 2000. His research interests include the chemical fixation of CO₂ in high

avoidance relative to the BAT and needs to be considered in terms of its life cycle.

The industrial-scale production of isocyanates, key building blocks in the manufacture of polyurethanes, is based on the reaction of the highly toxic gas phosgene and primary diamines (Scheme 1). This represents the principal industrial use of phosgene, a feedstock produced from chlorine and CO. Replacing phosgene with CO₂ (Scheme 1), therefore, constitutes an appealing strategy.¹⁵



Scheme 1 Traditional and proposed (dashed arrow) route to polyurethanes.

Polyurethanes are used in a diverse set of applications, ranging from foam structural materials to artificial hearts. Due to the diverse chemical functionality that can be introduced into these starting materials, numerous urethane-based polymers have been synthesized to cover a broad range of physical properties.¹⁶ A recent growth area has been in applications related to energy conservation, such as insulation foams and lightweight, non-rusting automobiles.

The alternative pathway to polyurethanes using CO₂ as a feedstock, as proposed by Aresta and Quaranta,¹⁵ is examined here in terms of the three sustainability criteria described above. The replacement of phosgene by more environmentally benign systems involving CO₂ is highly appealing, especially as it also avoids the use of chlorine and CO (Scheme 1). For example, Alba *et al.* reported the nickel-catalyzed dehydrative transformation of primary amines, alcohols, and CO₂ directly to urethanes.¹⁷ Under these conditions, the isocyanate step is avoided, and all reagents are introduced into the product using a catalytic process.

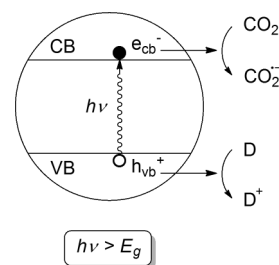
The elimination of multiple steps in the production of polyurethanes using CO₂ as a feedstock would lead to net negative CO₂ fixation, since the life cycle of the product has lower CO₂ emissions associated with it than equivalent products produced using the BAT. The magnitude of the CO₂ fixation potential is determined by the energy efficiency of isocyanate production from the diamine and CO₂ or, in the case of polyurethanes prepared in one step from CO₂, the diamine, and the diol. Ideally, the process would proceed at room temperature and/or as a photocatalytic system driven by sunlight. The fact that polyurethanes are increasingly being used to improve energy efficiency (*e.g.*, insulation and lightweight automobiles) also constitutes a net gain in terms of CO₂ fixation potential when compared to alternative plastics that could be manufactured with CO₂ as a feedstock.

The sequestration potential of CO₂ chemically incorporated into polyurethanes is high in terms of the length of time, estimated

in terms of hundreds of years, that the carbon is stored in this sink before being reemitted to the atmosphere. The total global production of methylene diphenyl diisocyanate, the most commonly used diisocyanate in polyurethane manufacturing, is approximately 2×10^6 tons per year.¹⁸ If this world supply were achieved using CO₂ as a feedstock instead of phosgene, it would account for approximately 2×10^5 tons of carbon (two moles of carbon per mole of methylene diphenyl diisocyanate) per year, or 0.003% of the approximately 7×10^9 tons of carbon emitted to the atmosphere as CO₂ due to anthropogenic activities.¹ Thus, the carbon sequestration potential for this technology is limited.

Semiconductor photocatalytic activation and fixation of CO₂

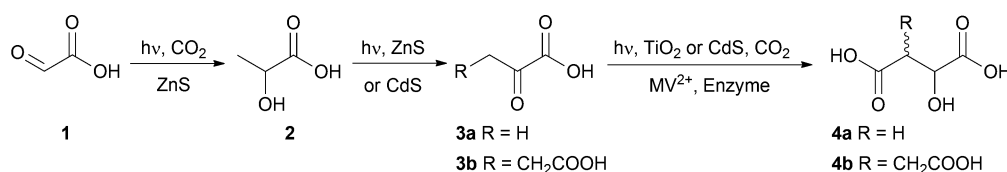
Photoexcitation of a semiconductor with light of an energy greater than or equal to the bandgap energy, E_g , results in the promotion of an electron (e_{cb}^-) from the valence band (VB) to the conduction band (CB) with the concurrent formation of a hole at the valence band (h_{vb}^+).¹⁹ In wide bandgap semiconductors, the transient electrons and holes can have high reduction and oxidation potentials, respectively. Electron and hole transfer reactions at the semiconductor surface can occur with suitable electron donors (D) and electron acceptors (A) to form radical ions as illustrated by Scheme 2. Net electron transfer occurs when the photogenerated states are trapped by a surface-bound chemical species²⁰ rather than undergoing a non-productive direct or indirect electron-hole recombination. Charge carrier trapping, which is determined by both thermodynamic and kinetic constraints, can lead to highly productive chemistry.



Scheme 2 Schematic representation of heterogeneous photochemical one-electron reduction of CO₂ on the surface of a suitable semiconductor.

The quantum yield of the photoreaction shown in Scheme 2 is governed by the efficiency of three processes:²¹ (1) photogeneration of the e_{cb}^-/h_{vb}^+ pair; (2) interfacial electron transfer between the semiconductor surface and the adsorbed reactants; and (3) transformation of the reduced/oxidized intermediates to first generation products. Coupling two semiconductors with the appropriate energy levels can increase the efficiency of charge separation and, hence, the first factor. The efficiency of the second process can be enhanced through the use of photoinactive supports such as silica, which can increase surface area and reactant adsorption kinetics. Both of the first two processes can be influenced dramatically by minor surface modifications of the semiconductor. The third factor is controlled by the reactivity of intermediate radicals and radical ions and, therefore, is less amenable to control.

The one electron reduction of CO₂ to its radical anion, CO₂^{•-}, (Scheme 2) is characterized by a large and negative reduction



Scheme 3 Semiconductor photocatalyzed fixation of CO₂ in metabolic intermediates. The photoproduction of lactic acid **2** from glyoxylic acid **1** is an eight electron reduction and occurs in 15% yield.³³ Lactic acid is photoreduced to pyruvic acid **3a**,^{33–34} which can fix another equivalent of CO₂ in the presence of a semiconductor photocatalyst, methyl viologen (MV²⁺), and malic enzyme to afford lactic acid **4a**.³⁴ In a related system, the photocatalytic fixation of CO₂ in oxoglutaric acid **3b** to produce isocitric acid **4b** occurs in the presence of CdS, MV²⁺, and isocitrate dehydrogenase.³²

potential, $E^\circ = -1.97$ V *versus* the normal hydrogen electrode (NHE) in *N,N*-dimethylformamide (-2.21 V *versus* the saturated calomel electrode, SCE).^{22–24} The unfavorable nature of this process is due to the thermodynamic stability of the CO₂ molecule and the energy required for a stereochemical change in geometry from a linear to a bent configuration. The transient radical anion is highly reactive and is known to rapidly undergo disproportionation to carbonate and CO,²⁵ as well as dimerization to oxalate.^{25–26} Multiple-electron reduction of CO₂ is more thermodynamically favorable. Typical reduction products are CO (2 electron reduction), formic acid (HCOOH, 2 electron reduction), elemental C (4 electron reduction), formaldehyde (HCHO, 4 electron reduction), methanol (CH₃OH, 6 electron reduction), and methane (CH₄, 8 electron reduction).²⁷ However, these multi-electron reductions often have kinetic limitations that make them difficult to achieve in practice with high efficiencies and selectivity.

Few photoactive semiconductors have sufficiently negative conduction band potentials to effect the one electron reduction of CO₂. In addition, the photocatalyst should be active to visible radiation ($\lambda > 400$ nm) in order to use the solar spectrum. The first report of photoelectrochemical reduction of CO₂ dates back over 30 years, and used a single crystal of zinc-doped p-type gallium phosphide as the photoelectrode.²⁸ The observed reaction products were HCOOH with traces of HCHO and CH₄. Inoue *et al.* subsequently examined the photoelectrocatalytic reduction of CO₂ in aqueous suspensions of semiconductor powders.²⁹ Six semiconductors were evaluated and HCOOH, HCHO, and CH₃OH were the main organic products observed. Henglein achieved an impressive quantum efficiency of 80% for the photocatalytic reduction of CO₂ to HCOOH by ZnS colloids, with the concomitant oxidation of sulfite to sulfate.³⁰ One of the earliest successful photoelectrochemical systems for the reduction of CO₂ was based on an InP semiconductor/methyl viologen (MV)/formate dehydrogenase (FDH) enzyme system.³¹ Light from a tungsten-halogen lamp illuminated InP, reducing MV²⁺ to MV⁺. The MV⁺ served as a mediator, reducing the FDH enzyme, which subsequently reduced dissolved CO₂ to HCOOH with current efficiencies between 89–93% and 21,000 turnovers.

A number of studies have examined the semiconductor-catalyzed photolytic fixation of CO₂ in carboxylic acids that make up metabolic intermediates in important cellular processes such as the reductive tricarboxylic acid (rTCA) cycle. The role of the semiconductor catalyst in these systems is to absorb the incident UV-visible radiation and generate energetic conduction-band electrons that are subsequently injected into a suitable redox cycle. Inoue *et al.* coupled CdS (photocatalyst) to methyl viologen (electron mediator) and isocitrate dehydrogenase (reaction catalyst) to fix

CO₂ in oxoglutaric acid **3b** to produce isocitric acid **4b** (R = -CH₂CO₂H, Scheme 3).³²

Inoue *et al.* also developed a system based on TiO₂ and CdS coupled to MV and malic enzyme to convert lactic acid **2** to malic acid **4a** *via* pyruvic acid **3a** (R = H, Scheme 3).³⁴ Lactic acid acted as the hole scavenger and was oxidized to pyruvic acid, which subsequently was carboxylated by malic enzyme to afford malic acid. Both of these examples involve carboxylation of the methylene group adjacent to an α -keto acid. More recently, Guzman and Martin have shown that glyoxylate **1** can be methylated to produce lactate in 15% yield (Scheme 3), an entry-point molecule in the rTCA.³³ In this photocatalytic reaction, the methyl unit is derived from CO₂ *via* an eight-electron reduction on the surface of ZnS colloids. While these CO₂ photofixation reactions are appealing, most of the carbon in the products originates from sources independent of CO₂.

C_x ($x \geq 2$) Compounds from CO₂ *via* semiconductor photocatalysis

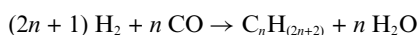
With an annual budget of 178,000 TW (1 TW = 10¹² W), incoming solar radiation makes up the major source of energy on earth.³⁵ Approximately 100 TW of this energy is used in biological photosynthesis (400 nm < λ < 700 nm) along with water to reduce CO₂ to a series of organic compounds that serve as the building blocks for life. Models integrating marine and terrestrial contributions estimated a global net primary production of 104.9 Pg (1 Pg = 10¹⁵ g) of carbon per year.³⁶ The maximum theoretical efficiency of solar energy to biomass conversion has been estimated at 4.6% for C3 photosynthesis (30 °C, 380 ppmv CO₂) and at 6% for C4 photosynthesis.³⁷ Photosynthesis occurs under mild conditions and employs highly organized biochemical catalysts where the participation of metal reaction centers is instrumental.¹⁰ First generation organic compounds formed in the reductive biological fixation of CO₂ vary between organisms, but common products include C₃ monosaccharides (*e.g.*, glyceraldehyde), C₄ carboxylic acids (*e.g.*, malate), C₅ monosaccharides (*e.g.*, ribose), and C₆ monosaccharides (*e.g.*, glucose). Artificial photosynthesis is inspired from this intensely-studied natural system and aims to develop photocatalytic approaches towards preparing organic compounds from CO₂. Under the strategies discussed here, the organic compounds constitute valuable building blocks of industrial significance where all carbon in these C_x ($x \geq 2$) materials is derived from CO₂.

Photochemical and photoelectrochemical CO₂ fixation in C_x ($x \geq 2$) compounds also may have played a role in prebiotic synthesis, where simple inorganic and organic compounds were converted into more complex biological molecules of fundamental

importance in the origin and evolution of life. For instance, it has been postulated that photoelectrochemical reduction of CO₂ on MnS and ZnS surfaces, minerals that could have been abundant in an anoxic early Earth, could have been involved in the prebiotic synthesis of acetate and propionate.^{38–39}

Photochemical Fischer–Tropsch chemistry

The Fischer–Tropsch (FT) process (*vide supra*) involves the catalytic conversion of CO and H₂ into hydrocarbons according to the following simplified stoichiometry:



As noted previously, many semiconductor photocatalytic or photoelectrochemical systems have been reported to produce CO and H₂ as simultaneous reaction products, thus it is conceivable that with appropriate photocatalytic arrays, the FT process may proceed under direct illumination with solar light to form higher alkanes than C₂.^{40–42} Many recent reports,^{43–53} however on the photocatalytic reduction of CO₂ on illuminated semiconductors show the simultaneous production of CO, H₂, CH₄ and CH₃OH with little evidence of further reduction to higher alkanes. In a rare exception, Bocarsly and colleagues^{54–55} have reported on the formation of methanol and several higher carbon-number alcohols (*e.g.*, ethanol, propanol, and butanol) in a selective photoelectrochemical reduction on illuminated p-GaP photoanodes, *via* participation of a reduced pyridyl radical, and later on other photoanodes such as p-GaAs and p-GaAsP₂.

One of the ambitious goals of artificial photosynthesis is to use relatively inexpensive, earth-abundant semiconducting materials that absorb in the visible portion of the solar spectrum. Doped and modified TiO₂ and related materials have been explored extensively^{56–57} in this regard in spite of their known limitations. In addition, TiO₂ has also functioned as a catalyst support for conventional, high temperature conversion of CO and H₂ into hydrocarbons. There are several reports^{58–60} of the photocatalytic reduction of CO₂ on TiO₂ that show the formation of C₂H₄, C₂H₆, ethanol, acetone, and acetaldehyde. At Caltech, we have observed the simultaneous production of CO, H₂, CH₃OH, CH₄, C₃H₈, and C₄H₁₀ on hybrid CdS/TiO₂ composites under visible light irradiation and with photoelectrochemical systems involving Bi-doped TiO₂ photoanodes coupled with Cu or brass cathodes. The product distributions were confirmed by isotopic labeling using ¹³CO₂ as the carbon source. Similar results are obtained photoelectrochemically. These observations need to be confirmed under a broad range of reaction conditions.

The chemical speciation of CO₂ in water needs to be well-defined, as aquated CO₂ (CO_{2,aq}), H₂CO₃, HCO₃[–], and CO₃^{2–} may be important species requiring close interaction with the illuminated semiconductor surface. The detailed surface-bound speciation and modes of bonding that allow for electron transfer from the conduction band or from trapped surface states (*e.g.*, >Ti(III)OH) has yet to be unraveled. The role of these critical surface interactions has attracted the attention of the theoretical and computational chemistry community.^{61–63} Indrakanti *et al.*⁶¹ argue that the conduction band electrons cannot be transferred directly to CO₂, but that the oxygen vacancies on the surface of TiO₂ are possible energetically favorable sites for electron transfer to CO₂.

Since there is strong evidence for the formation of CO and H₂ during the photocatalytic reduction of CO₂/HCO₃[–] systems, one must consider the solubility of CO and its tendency to remain within the electrical double layer surrounding the photocatalyst in order to achieve additional steps in the overall reduction. The limited solubility of CO in water may constrain the subsequent reductions needed to form higher carbon number compounds under ambient conditions. For example, the Henry's Law constants for CO₂, CO and H₂ in units of L-atm mol^{–1} are 3.4 × 10^{–2}, 9.5 × 10^{–4}, and 7.8 × 10^{–4}, respectively.⁶⁴ Since CO₂ is in equilibrium with HCO₃[–] (pK_{a1} = 6.3; pK_{a2} = 10.4), the solubility of CO₂ is not a primary issue, but when both CO and H₂ are produced *via* photoreduction, they very quickly form bubbles with sufficient size and buoyancy to rapidly escape from the liquid phase into the gas phase. One challenge going forward is to increase the solubility of both CO and H₂ in order to allow for further electron transfer to take place near the semiconductor surfaces, or to use reactors under pressure in the absence of a head space.

C₂ Hydrocarbons

Higher hydrocarbons may be produced from CO₂ and semiconductor photocatalysis *via* processes that do not necessarily involve FT chemistry, although the detailed mechanisms are not usually known. A 1987 report from the Grätzel group demonstrated that the eight-electron reduction of CO₂ in the presence of H₂ to produce CH₄ and water (Sabatier reaction) could be achieved selectively and under mild conditions (room temperature and atmospheric pressure) using UV-visible irradiation (λ > 310 nm) and highly dispersed Ru/RuO_x loaded onto a TiO₂ support as the photocatalyst.⁶⁵ High turnover frequencies (1.4 × 10^{–3} s^{–1}) were observed in this system, which appeared to involve the four-electron reduction of CO₂ to produce an intermediate Ru–C surface species. The reaction is driven by photogenerated conduction band electrons in the TiO₂ support. In parallel efforts, Willner *et al.* successfully photoreduced CO₂ to CH₄ and C₂ HCs under mild conditions using an aqueous system, visible light (λ > 400 nm), Ru or Os colloidal catalysts, and a number of electronic relays.²⁷ Of particular note was the production of H₂, C₂H₆, and C₂H₄ along with CH₄. The highest observed rates of C₂H₆ and C₂H₄ formation, 0.18 and 0.36 μL h^{–1}, respectively, were obtained with Ru colloids and a Ru(II) trisbipyrazine photosensitizer. The C₂ HCs were thought to form *via* intermediate Ru carbene complexes, Ru=CH₂. Unfortunately, the quantum yields and turnover frequencies for this system were modest.

Cook *et al.* found that photolysis of dispersed colloidal p-SiC/Cu mixtures in the presence of CO₂ generated C₂H₆ and C₂H₄ as well as CH₄.⁶⁶ The C₂ HC formation rates were dependent on the electrolyte pH and were highest at pH 5, notably 3.9 and 2.3 μL h^{–1} g^{–1} for C₂H₄ and C₂H₆, respectively. The reduction occurred on the surface of the Cu particles with the energetic conduction band electrons being shuttled to the catalyst from the photoexcited SiC semiconductor. When Cu-loaded TiO₂ powders were suspended in water and photolyzed in the presence of CO₂ at 5 MPa of pressure, CH₄, C₂H₄, C₂H₆, and H₂ were formed.⁶⁷ At the optimal Cu (5% w/w)/TiO₂ concentration, the yields of CH₄ and C₂H₄ were 22 and 26 μL g^{–1}, respectively. The maximum yield of C₂H₆ of 2.7 μL g^{–1} was obtained at

Cu (1% w/w)/TiO₂. The authors speculate that carbon radicals are formed on the surface of the TiO₂ catalyst, and subsequently are reduced to methylene radicals ($\cdot\text{CH}_2$) by TiO₂/Cu. Ethylene is formed by the combination of two of these surface species.

Using a different approach, Inoue *et al.* prepared TiO₂ nanoparticles (particle size 3–5 nm) embedded in SiO₂ matrices using a sol–gel method and showed that these supported semiconductors photoreduced ($\lambda > 270$ nm) CO₂ to C₂H₄ with a maximum quantum efficiency of 2.3% (Ti/Si ratio of 0.027), along with HCOOH and CH₄, with quantum efficiencies of 14% and 3.4%, respectively.⁶⁸ Lo *et al.* investigated the aqueous photocatalytic reduction of CO₂ on mixed TiO₂ ($\lambda > 365$ nm) and ZrO₂ ($\lambda > 254$ nm) semiconductors adsorbed on glass beads in the presence of H₂.⁶⁹ Three principal reduction products were observed: CH₄, CO, and C₂H₆ with yields of 8.21, 0.28, and 0.20 $\mu\text{mol g}^{-1}$, respectively. The proposed mechanism for C₂H₆ formation involves stepwise reduction of CO₂ $^{\cdot-}$ to HCHO, *via* HCOOH, affording adsorbed methyl radicals ($\cdot\text{CH}_3$). Combination of two of these intermediates affords C₂H₆.

A number of photoelectrochemical systems also have been used to reduce CO₂ to C₂ HCs. Kaneco *et al.* showed that Ni-modified p-InP photoelectrodes could be used to produce C₂H₄, along with other C₁ reduction products, albeit with current efficiencies below 1%.^{70–71} Nguyen and colleagues used optical fibers coated with Cu(II)- and Fe(III)-doped TiO₂ and a Ru(II)-based dye sensitizer (N3) to reduce CO₂ to CH₄ (0.85 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$) and C₂H₄ (0.56 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$) during UV irradiation.^{72–73} The authors showed that CO₂ activation resulted from direct bandgap excitation of TiO₂, not sensitized visible excitation. With natural sunlight, the N3 dye increased the photoproduction of CH₄, but C₂H₄ was not produced.⁷² In UV-irradiated (250–450 nm) fiber systems with Cu and Fe co-doped TiO₂, photoreduction of CO₂ and gas-phase H₂O led to formation primarily of CH₄ and C₂H₄, with the highest C₂H₄ production rate of 0.58 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ found for Cu and Fe loadings of 0.5% wt each.⁷³ The coated-optical fiber configuration increased photoyields by an order of magnitude over identical photocatalysts on flat glass plates.

Ethanol

Few reports have appeared in the literature on the formation of C₂ alcohols and aldehydes from the photocatalytic reduction of CO₂. In a 1987 report, Yamamura *et al.* first observed ethanol from CO₂ *via* photolysis using a variety of semiconductor catalysts, ranging from SiC to metal-coated ZnSe powders.⁷⁴ The highest yield (180 $\mu\text{mol g}^{-1}$) was obtained with SiC after 8 h of irradiation at pH 3.6. A tenfold lower yield was obtained with ZnSe powder, which required a metal coating to show activity. Twenty years later, multi-walled carbon nanotube supported TiO₂ catalysts prepared by a sol–gel method were found to reduce CO₂ to ethanol upon UV-visible irradiation over 5 h with yields up to 149.4 $\mu\text{mol g}^{-1}$.⁶⁰ More recently, Liu *et al.* used monoclinic BiVO₄ suspensions in an aqueous system to photoreduce ($\lambda > 400$ nm) CO₂ to ethanol at rates as high as 406.6 $\mu\text{mol h}^{-1}$.⁷⁵ In a typical experiment 0.2 g of catalyst was used with photolysis reactions times of 80 min, affording yields of *ca.* 2,700 $\mu\text{mol g}^{-1}$, significantly higher and in a shorter period of time than in previous reports.

C₂–C₄ Carboxylic acids

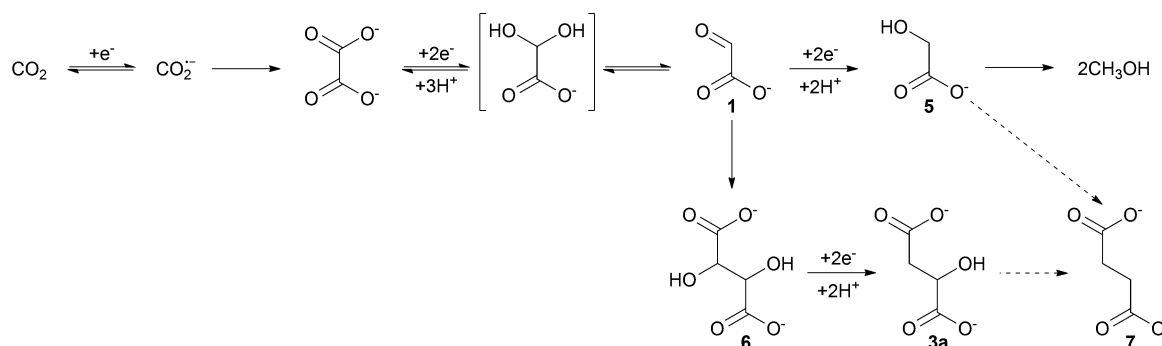
The dimerization of CO₂ $^{\cdot-}$ to oxalate (C₂O₄ $^{2-}$) is a well-established process^{22,76} and, therefore, oxalic acid is an expected by-product in the one electron photoreduction of CO₂. In other systems, C₂O₄ $^{2-}$ can be formed by the oxidation of HCOOH, possibly in a complementary process to the dimerization of CO₂ $^{\cdot-}$. For example, Kisch and Lutz investigated the photolysis of bicarbonate -used as a CO₂ equivalent- catalyzed by supported CdS and using sulfite as the sacrificial electron donor.²¹ The products observed in silica-supported CdS systems were HCHO and HCOOH in the 15–35 μM range, and C₂O₄ $^{2-}$ in the 1–8 μM range. HCHO was formed directly and not from the two electron reduction of HCOOH. The formation of C₂O₄ $^{2-}$ proceeded both by dimerization of CO₂ $^{\cdot-}$, which increased linearly with surface coverage of CdS, as well as by the oxidation of HCOOH by valence band holes. Oxalate is a feedstock in the production of dimethyl oxalate, which in turn is used to make other useful industrial chemicals, such as methyl glycolate. Recently, Angamuthu *et al.* reported a dinuclear copper complex that spontaneously captured CO₂ from air to selectively form an oxalate-bridged Cu(II) tetramer.⁷⁷ In an electrocatalytic cycle, the activation of CO₂ and catalytic formation of C₂O₄ $^{2-}$ occurred with oxidation of the Cu(I) complex by CO₂ upon binding, coupling of four bound CO₂ $^{\cdot-}$ to form two equivalents of C₂O₄ $^{2-}$, and Cu(II) electroreduction back to Cu(I) as the rate-limiting step. While the system does not use photolysis to drive the reduction, it is included here because it represents a rare case of selective CO₂ conversion to C₂O₄ $^{2-}$ using an electrocatalyst.

The photosynthesis of C₂ and C₄ acids from CO₂ and colloidal semiconductor catalysts has been studied and developed extensively by Eggins and coworkers.^{78–81} Product formation was rationalized according to Scheme 4.

Initial photochemical (320 < λ < 580 nm) experiments involved aqueous colloidal CdS suspensions, a suitable electrolyte, and gas-phase CO₂.⁷⁸ Product analyses were carried out by HPLC, GC, and colorimetry. Glyoxylate **1** yields as high as 116 $\mu\text{mol dm}^{-3}$ (quantum efficiency 1.03×10^{-3}) were observed after 36 h at pH 6 and in the presence of 0.1 M tetramethylammonium chloride (electrolyte) and 5 mM sulfite (hole acceptor). Acetate (up to 40 $\mu\text{mol dm}^{-3}$) and trace acetaldehyde also were observed as well as other C₁ reduction products. No C₂O₄ $^{2-}$ was observed, but was invoked as a likely intermediate. Building on these results, Irvine *et al.* found that the quantum efficiency of the process could be increased eighteen fold when hydroquinone was used as a sacrificial electron donor.⁷⁹ Formate was the primary reaction product in these studies, and glyoxylate **1** levels decreased with time and were associated with an increase in tartrate **6** concentrations (see Scheme 4). Experiments with a flat-plate solar collector (area $5 \times 10^{-3} \text{ m}^2$) and CdS (2 g) suspended in water (500 mL) at pH 4 with continuous bubbling of CO₂ over 96 h yielded HCOOH (8.4 μM) with a modest quantum efficiency of 2.8×10^{-5} .

Upon switching the photocatalyst from CdS to ZnS, Eggins and colleagues identified C₂O₄ $^{2-}$ as the main reaction product (yields up to 2.3 mM), along with glyoxylate **1** and glycolate **5** as the other principal C₂ acids.⁸⁰ The formation of tartrate **6** was obtained in up to 16 μM yield as the only C₄ acid.

Throughout these studies, tetraalkylammonium ions supported the photocatalytic reduction of CO₂, presumably by adsorbing to the surface of semiconductor particles and excluding



Scheme 4 Semiconductor photocatalyzed reduction of CO_2 to C_2 and C_4 acids.⁸¹ **1**, Glyoxylate; **5**, glycolate; **6**, *DL*-tartrate; **3a**, *DL*-malate; and **7**, succinate.

most of the water.⁸¹ This not only stabilized the colloids from photocorrosion, but also appeared to provide a microenvironment suitable for the buildup of $\text{CO}_2^{\bullet-}$ on the particle surface, leading to the oligomerization observed in the C_2 and C_4 products.

Zhang *et al.* photolyzed C(+IV) as bicarbonate -a surrogate for CO_2^- in the presence of MnS and ZnS and obtained HCOOH as the primary photoreduction product with quantum efficiencies as high as 4.2% and 10%, respectively.^{38–39} These studies also afforded acetate (MnS, 4 μM ; ZnS, 5 μM) and propionate (MnS, 15 μM ; ZnS, 8 μM) as secondary reaction products, potentially *via* the reaction of $\text{CO}_2^{\bullet-}$ with HCOOH. Eggin *et al.* observed up to 40 μM acetate during the photolysis of colloidal CdS particles in the presence of CO_2 and tetramethylammonium chloride, but not when ZnS was used as the photocatalyst.^{78,81}

Conclusions

The production of C_x ($x \geq 2$) fuels and industrial chemical building blocks from CO_2 and solar radiation using semiconductor photocatalysts holds significant promise, but numerous technical hurdles remain. The quantum efficiencies, reaction yields, and product selectivities of most systems reported in the literature require considerable improvements to become practical even on a pilot scale. A better understanding of the processes that underpin this complex chemistry is required to allow better predictability and, hence, systematic design of approaches that overcome these limitations. Most of the research to date has been limited to the fixation of CO_2 in C_1 compounds, and C_x ($x \geq 2$) products largely have been overlooked. In fact, it is likely that C_x products are formed in many of the numerous reports on C_1 CO_2 photoreduction products, but were not detected by the techniques used in product analysis.

Finally, Yang *et al.*⁸² have argued based on their experimental observations that “carbon residues left over from the synthesis of TiO_2 and other metal oxide semiconductors (*e.g.*, from metal alkoxides) are involved in the photocatalytic reduction of CO_2 to carboxylic acids, alcohols, and alkanes”. These experiment “artifacts may have influenced or accounted for the reported product arrays and rates of artificial photosynthesis reported in many studies in the literature.” These potential artifacts need to be considered in future research.

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